FABRICATION AND CHARACTERIZATION OF EXPERIMENTAL NANOCOMPOSITES FOR DENTAL RESTORATION

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UNIVERSITI SAINS MALAYSIA

2012

ACKNOWLEDGEMENT

First and foremost, I would like to express my sincere gratitude to my supervisor, Dr. Dasmawati Mohamad for her continuous support and guidance throughout my study. I owe her a lot for spending her time and effort to evaluate my research papers and thesis prior to submission.

I wish to express my warm and sincere thanks to my co-supervisor, Assoc. Prof. Dr. Hazizan Md Akil at School of Materials and Mineral Resources for his precious advices, motivation and ideas in this project.

My sincere thanks also go to the lab technologists and technicians at the School of Dental Sciences and School of Materials and Mineral Resources for providing me the facilities of testing and the constant assistance during my lab work.

I would like to extend my gratitude to the Universiti Sains Malaysia for the financial support given through the RU Grant 1001/PPSG/813012 and Incentive grant 1001/PPSG/8122004 and also for the USM fellowship.

Last but not the least, I would like to thank my beloved family especially my husband, Ahmad Fikri Md Sharif, our little princess, Izzah Balqis Ahmad Fikri and also my parents, Tuan Rahim Tuan Mat and Tuan Asma Tuan Iberahim for supporting me spiritually throughout my life.

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LIST OF ABBREVIATIONS

ADA	American Dental Association
AFM	atomic force microscope
APTES	3-aminopropyltriethoxysilane
ATR	attenuated total reflectance
BisEMA	ethoxylated bisphenol-A-dimethacrylate
BisGMA	bisphenol glycidyl methacrylate
CQ	camphorquinone
DC	degree of conversion
DMAEMA	N,N-dimethylaminoethyl methacrylate
e.g.	for example
FDA	Food and Drug Administration
FESEM	field emission scanning electron microscopy
FTIR	fourier transform infrared spectroscopy
GPS	γ-glycidoxypropyltrimethoxysilane
i.e.	that is
ISO	International Organization for Standardization
LCU	light curing unit
LED	light emitting diodes
PAC	plasma-arc lights
QTH	quartz tungsten halogen
RDB	remaining carbon-carbon double bonds
TEGDMA	triethylene glycol dimethacrylate
TEOS	tetraethylorthosilicate
UDMA	urethane dimethacrylate

USM	Universiti Sains Malaysia
UTM	universal test machine
UV	ultraviolet
γ-MPS	γ-methacryloxypropyltrimethoxysilane

LIST OF SYMBOLS

Mw	molecular weight
2D	two dimensional
3D	three dimensional
R_a	surface roughness
B/T	bottom/top
σ_{FS}	flexural strength
σ_{CS}	compressive strength
E	modulus
WS	water sorption
S	solubility
ΔV	volumetric difference between before and after cure
p_1	peak area at 1637 cm^{-1}
p_2	peak area at 1608 or 3373 cm^{-1}
m_1	conditioned mass
m_2	mass of specimen after immersion in water for 7 days
m_3	mass of the reconditioned specimen

FABRIKASI DAN PENCIRIAN KE ATAS NANOKOMPOSIT UJIKAJI UNTUK TAMPALAN GIGI

ABSTRAK

Pada masa ini, komposit tampalan gigi telah menjadi pilihan utama di kalangan pesakit disebabkan oleh sifat estetik dan juga ketahanan mereka. Harga komposit yang tinggi, di samping permintaan yang semakin meningkat oleh pesakit telah menyebabkan para penyelidik ingin menghasilkan produk tempatan yang setaraf dengan komposit komersial yang sedia ada. Baru-baru ini, pengisi silika nano yang monosebaran, berbentuk sfera dengan saiz dalam lingkungan 10-20 nm telah berjaya disintesis melalui proses sol-gel dan berpotensi untuk digunakan dalam fabrikasi komposit pergigian. Oleh itu, kajian ini dijalankan untuk menfabrikasi dan mencirikan komposit nano ujikaji pergigian yang dihasilkan daripada pengisi silika nano yang disintesis. Komposit pergigian, diberi nama sebagai komposit nano ujikaji 1 (ENC1) dan komposit nano ujikaji 2 (ENC2) dengan dua kandungan pengisi yang berbeza, masing-masing dengan berat 30 dan 35 % difabrikasi, diacuankan dan dipempolimerkan dengan menggunakan unit pematangan cahaya selama 40 s. Sifat-sifat yang diuji termasuklah kekuatan lenturan, modulus, kekuatan mampatan, kekerasan mikro, darjah penukaran, pengecutan isipadu, penyerapan air, kebolehlarutan, kekasaran permukaan serta pengedaran pengisi. Data yang diperoleh dianalisis secara statistik menggunakan Anova Sehala dengan tahap signifikan p=0.05. Pelbagai jenis komposit komersial iaitu Filtek™ Z350 (komposit nano), Spectrum® TPH®3 (campuran mikro), Z100™ (campuran) and Durafill® VS (berisi mikro) telah dipilih untuk membandingkan sifta-sifat mereka dengan komposit nano ujikaji. Sifat-sifat komposit juga dirujuk kepada keperluan ISO dan ANSI/ADA No.

27. Daripada keputusan yang diperolehi, boleh dirumuskan bahawa komposit nano uji kaji dan komposit komersial memenuhi keperluan ISO dan ANSI/ADA No. 27. Persamaan sifat-sifat boleh didapati di antara komposit-komposit nano ujikaji dan Durafill VS (komposit berisi mikro) berhubung dengan kekuatan lenturan, modulus, kekuatan mampatan, kekerasan dan juga kekasaran permukaan. Sifat-sifat ini mencukupi untuk diaplikasikan pada penampalan anterior. Walau bagaimanapun sifat komposit ujikaji masih rendah berbanding dengan komposit pergigian posterior (Filtek™ Z350, Spectrum® TPH®3 dan Z100™) terutamanya kekuatan lenturan, modulus, kekerasan, pengecutan dan penyerapan air. Membandingkan kedua-dua komposit nano ujikaji, ENC2 mempamerkan sifat yang lebih baik kecuali kekuatan mampatan. Secara keseluruhannya, faktor utama yang menyumbangkan kepada sifat-sifat komposit pergigian adalah pengisi bukan organik termasuklah kandungan, saiz, morfologi dan pengedaran pengisi. Komposit berpengisi tinggi mempamerkan sifat-sifat yang lebih baik berbanding komposit berkandungan pengisi rendah. Silika nano yang disintesis boleh menjadi sebagai satu pilihan untuk digunakan dalam pembuatan komposit pergigian, namun kebimbangan turut timbul berkenaan dengan masalah untuk mencapai pembebanan pengisi yang tinggi, di mana menghadkan penggunaannya untuk membuat komposit anterior.

FABRICATION AND CHARACTERIZATION OF EXPERIMENTAL NANOCOMPOSITES FOR DENTAL RESTORATION

ABSTRACT

Currently, restorative dental composites have become preferred among patients due to their aesthetic characteristic and also their durability. The high costs of composites, as well as the rising demand by patients have lead researchers to produce a local product with equivalent standard as compared to the commercially available dental composites. Recently, monodispersed, spherical silica nanofillers with a size range of 10-20 nm were successfully synthesized via a sol-gel process and have a great potential to be used in fabrication of dental composites. Therefore, this present study was carried out to fabricate and characterize the experimental dental nanocomposite from the synthesized nanosilica fillers. Dental composites, namely experimental nanocomposite 1 (ENC1) and experimental nanocomposite 2 (ENC2) with two different filler content, 30 and 35 wt% respectively were fabricated, molded and polymerized with a light curing unit for 40 s. The properties that were tested including their flexural strength, modulus, compressive strength, micro hardness, degree of conversion, volumetric shrinkage, water sorption, solubility, surface roughness as well as filler distribution. The data obtained were statistically analyzed with One-Way ANOVA with the level of significance p=0.05. Various type of commercial composites i.e. Filtek™ Z350 (nanocomposite), Spectrum® TPH®3 (microhybrid), Z100™ (hybrid) and Durafill® VS (microfilled) were chosen to compare their properties with the experimental nanocomposites. The properties of composites were also referred to the ISO and ANSI/ADA No. 27 requirements. From

the results obtained, it can be summarized that the experimental nanocomposites and commercial composites complied with the ISO and ANSI/ADA No. 27 requirements. Similar properties can be found between experimental nanocomposites and Durafill® VS (microfilled composite) regarding their flexural strength, modulus, compressive strength, hardness and also surface roughness. These properties are sufficiently to be applied at the anterior restoration. However the properties of experimental nanocomposites were still inferior compared with the posterior restorative composites (Filtek™ Z350, Spectrum® TPH®3 and Z100™) particularly in flexural strength, modulus, hardness, shrinkage and water sorption. Comparing both of experimental nanocomposites, ENC2 seems to have better properties compared with ENC1 except for compressive strength. Overall, the main factor that contributes to the properties of dental composites is inorganic fillers including their filler content, size, morphology and distribution. Highly filled composites exhibited excellent properties than the composites with low filler content. The synthesized nanosilica might be an option to be used for making a dental composite, however concerns also arise regarding their problem of achieving the high filler loading, which limit their application only for making anterior composite.

CHAPTER 1
INTRODUCTION

1.1 Background of the study

Dental restorative materials are specially fabricated materials designed for dental restorations, in which they are used to repair damaged or decayed tooth that occurs as a result of dental caries. Dental amalgams have been used for over 150 years and still being used, particularly in large cavities due to their excellent mechanical properties and durability. However, the development of tooth-coloured dental composites for the treatment of dental caries has resulted in a high demand by patients. Dental composites are types of polymer composite which are viewed as an attractive alternative to amalgam restorations due to their aesthetic characteristics and their ability to adhere to the tooth substance when using with resin bonding agent. Concern has also been raised over the mercury toxicity in dental amalgam, in which possible symptoms can be happened for patient with amalgam restoration including allergic reactions, kidney failure, lichen planus disease and also neurological and psychological effects e.g. Alzheimer disease, Parkinson disease and multiple sclerosis (Scientific Committee on Emerging and Newly Identified Health Risks, 2008).

Basically, a dental composite is composed by four major components: polymer matrix, inorganic fillers, filler-matrix coupling agent and photoinitiator system (Kim and Shim, 2001). Recent improvements have been achieved mainly through organic monomer discovery, modification in formulation and filler technology, advances in light curing equipment and introduction of efficient photoinitiators (Soh *et al.*, 2006). Despite of these achievements, continued efforts are still on going to improve the

performance of current composites regarding their mechanical properties, aesthetic properties as well as polymerization shrinkage.

Restorative dental composites are traditionally classified according to their filler particle sizes which are macrofilled composites (8-12 μm), small particle composites (0.5-3 μm), microfilled composites (0.04 μm), hybrid composites (0.04 μm; 1-5 μm) (Anusavice, 2003) and recently, nanocomposites with filler size below than 100 nm have been introduced. The development of nanotechnology has gained a significant improvement in evolution of dental composites as they provide smoother surface with high translucency and polishability comparable to those of microfilled composites while their mechanical properties and wear resistance are equivalent to those of several hybrid composites (Mitra *et al.*, 2003).

Nanosilica fillers have gained popularity and widely used in preparing restorative dental composite. Silica fillers differ from the traditional, micron sized quartz and glass fillers, in which silica fillers can be size-controllable and also can be prepared in a range of nanometers in dimension (Kim *et al.*, 2007b, Jafarzadeh *et al.*, 2009). The use of nanosilica fillers in dental composite allows the material to be polished, therefore less wear and plaque accumulation will occur (Lakes, 2000).

One of the most important techniques used to prepare nanosilica fillers is by sol gel process. Nanofillers synthesized using this method was reported to have a distinct spherical shape with narrow size distributions (Nirschl, 2003, Jafarzadeh *et al.*, 2009). The extremely small nanosilica provide low visual opacity in unpigmented dental composites, which allow researchers to prepare wide shades and opacities of dental composites, and thus provide highly aesthetic restorations (Mitra *et al.*, 2003). Furthermore, spherical shaped of nanosilica particles tend to distribute the mechanical stress more uniformly than irregular shaped particles, which contribute to

improve mechanical properties (Tian *et al.*, 2008). The latest development in filler technology is nanomer and nanocluster produced by 3M ESPE for their nanocomposites, Filtek Supreme^{TM} and Filtek Z350^{TM}.

In oral environment, restorations are subjected to stresses from mastication action. The forces act on teeth and/or material producing different reactions that lead to deformation, which can ultimately compromise their durability over time (Wang *et al.*, 2003). Therefore, some characterizations on mechanical properties, shrinkage, water sorption and other related properties of dental composites must be carried out to prove their applicability and reability. The knowledge of these properties is essential to support the correct indication of new dental composite before applying the material in dental practice and to expect a long-term performance.

1.2 Statement of the problem

Inorganic fillers always been the main factor studied for the development and characterization of new dental composites. This can be seen by the high number of researchers who involved and focused in inventing a new type of filler, while they still prefer using the same resin monomers (Klapdohr & Moszner, 2005, Ruttermann *et al*., 2008).

Although the use of nanosilica fillers have proven to enhance various properties of dental composites, however, until now all commercial products are comprised with micron sized particles, clusters or prepolymerized fillers with only incorporated by small amount of nanosilica fillers (10-20 wt%) (Anusavice, 2003). From this viewpoint, a composite containing all sized nanofillers should be prepared to evaluate the effect of nano sized fillers on properties of dental composite. Recently, local researchers have successfully synthesized nanosilica fillers with a size range

10-20 nm by sol-gel process and resulted in relatively monodispersed with low agglomeration (Figure 1.1) (Jafarzadeh *et al.*, 2009). Incorporation of nanosilica fillers in preparing the new dental composite has a great potential in improving the properties of composites compared with the available dental composites at the market.

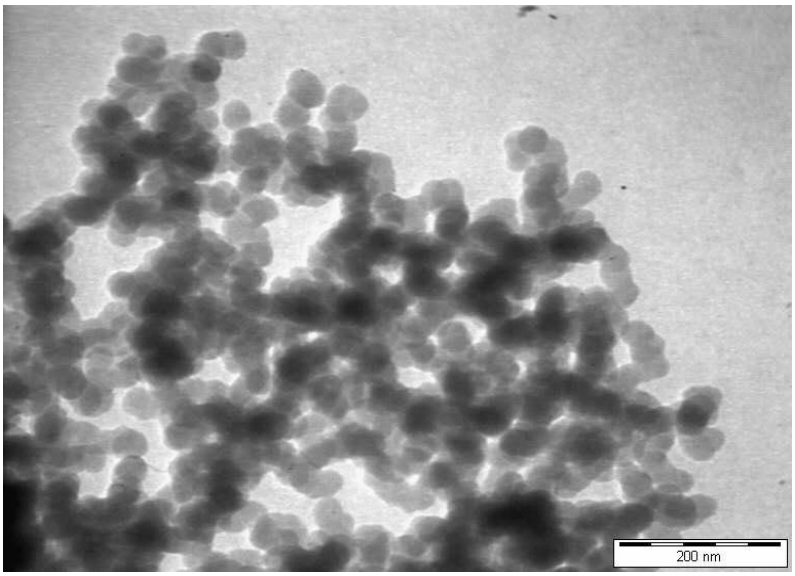


Figure 1.1: TEM image of silica nanofillers are relatively monodispersed

The high demand for dental composites has led to the emergence of various types of products claiming to be the new breakthrough in restorative composite. According to Table 1.1, the number of tooth-restoration at USM dental clinic in year 2009 is considerably high, which requires a high consumption of government expenditure per year. The price for a tube of 4 gram dental composite is ranged from RM100 to RM200, depending on the brand and type. In addition, all commercial dental composites are being manufactured in foreign country. All these reasons energized the local researchers to invent and produce a local restorative dental composite of equivalent standard which is affordable by our own community.

Table 1.1: Number of tooth-restoration and composites used at USM dental clinic in year 2009

Number of tooth-restoration	9260 cavities
Number of composite used (4g/tube)	930 tubes

Therefore, this study was conducted to prepare the experimental nanocomposites using nanosilica as fillers, and their characterizations were also evaluated. The properties that were tested including flexural strength, modulus, compressive strength, hardness, degree of conversion, shrinkage, surface roughness, water sorption, solubility as well as filler distribution.

1.3 Justification of the study

Due to the limited number and highly price of commercially available dental nanocomposites, involvement in this industry will contribute to the growth of nanocomposites market and also raise the country's economy. The end product has potential to replace the current applied commercial composites, which is indirectly will commercialize the local product and will reduce the cost of dental treatment. Utilization of synthesized nanosilica fillers towards the development of new restorative dental composite also helped in determining the advantages and disadvantages of nanosilica fillers in comparison with the current available fillers.

1.4 Objectives of the study

1.4.1 General objective:-

To fabricate and characterize the experimental dental nanocomposites based on synthesized nanosilica fillers and compare with commercial composites.

1.4.2 Specific objectives:-

1. To compare the mechanical properties of experimental dental nanocomposites with commercial dental composites.
2. To compare the volumetric shrinkage of experimental dental nanocomposites with commercial dental composites.
3. To compare the degree of conversion of experimental dental nanocomposites with commercial dental composites.
4. To compare the water sorption and solubility of experimental dental nanocomposites with commercial dental composites.
5. To compare the surface roughness of experimental dental nanocomposites with commercial dental composites.

1.5 Hypotheses:-

1. There is no significant difference of mechanical properties between experimental dental nanocomposites and commercial dental composites.
2. There is no significant difference of volumetric shrinkage between experimental dental nanocomposites and commercial dental composites.
3. There is no significant difference of degree of conversion between experimental dental nanocomposites and commercial dental composites.

4. There is no significant difference of water sorption and solubility between experimental dental nanocomposites and commercial dental composites.

5. There is no significant difference of surface roughness between experimental dental nanocomposites and commercial dental composites.

CHAPTER 2
LITERATURE REVIEW

2.1 Polymer composites for dental restoration

The introduction of polymer based composite technology since 1970s was one of the most significant contributions to the dentistry, allowing dental restorations to be more natural, tooth-like structure. Since their advent, these materials or better known as restorative dental composites have become increasingly popular and undergone significant development, which continues to improve the longevity of restoration (Bernardi *et al.*, 2008). Before the introduction of dental composites, dental amalgams have been used as a dental filling material for more than 150 years. Dental amalgam is a combination of alloy particles and mercury that contains about 50 % of mercury in the elemental form (Scientific Committee on Emerging and Newly Identified Health Risks, 2008). The mercury contained in amalgam however remains the unresolved controversies in dentistry which is being associated to the adverse effects on human health. Excellent aesthetic, acceptable mechanical properties and also the safety assurance possessed by dental composites has caused these materials to be promoted as an adjunct to or substitute for amalgams in the restoration of posterior dentition (Ferracane, 1995).

2.2 Performance standards for restorative dental composites

Product of restorative dental composites are required to meet the performance standards established by the Food and Drug Administration (FDA) or other appropriate standards from other authoritative bodies, such as those of the American Dental Association (ADA) and International Organization for Standardization (ISO). Specific data must be provided by manufacturer to demonstrate the safety and

efficacy of product before marketing. Manufacturer needs to submit premarket approval applications to FDA which then will be evaluated by the Dental Products Panel to determine whether the new product can be marketed (Anusavice, 2003). The list below is a recommended description relating with the physical and mechanical properties and biocompatibility of the product, which provided by FDA to the manufacturers and also the recommended test standards (Food and Drug Administration, 2005).

Table 2.1: Details to be given to FDA and the recommended test standards for restorative dental composites

Test	Recommended test standard
Compressive strength	ANSI/ADA Specification No. 27 for direct filling resins, ISO 9917:2003, Dentistry-Water-based cements
Flexural strength Elastic modulus Depth of cure Water sorption Solubility Radiopacity Curing time Working time Setting time	ISO 4049:2000(E), Dentistry—Polymer-based filling, restorative and luting materials
Filler particle distribution Surface hardness Intensity for curing Wavelength for curing	No standard
Biocompatibility	ISO 7405:1997(E), Dentistry - Preclinical evaluation of biocompatibility of medical devices used in dentistry

2.3 Definition of composite and composition of restorative dental composite

Composite material may defined as a compound of two or more distinctly different materials with properties that are superior or intermediate to those of the individual constituents (Anusavice, 2003). Restorative dental composites are complex, consist of a polymer matrix as organic phase, inorganic fillers as dispersed phase, filler-matrix coupling agent, and minor additives including polymerization initiators, accelerators, stabilizers and colouring pigments (Figure 2.1).

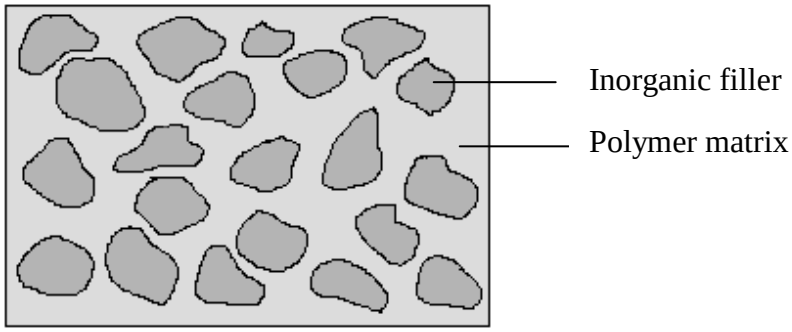


Figure 2.1: Structure of a restorative dental composite

2.3.1 Polymer matrix

Most restorative dental composites use monomers that are aromatic or aliphatic diacrylates. Bisphenol glycidyl methacrylate (BisGMA), urethane dimethacrylate (UDMA), and triethylene glycol dimethacrylate (TEGDMA) and ethoxylated bisphenol-A-dimethacrylate (BisEMA) are the common dimethacrylates used in dental composites (Figure 2.2 a-d) (Anusavice, 2003).

BisGMA possesses many advantages, such as high molecular weight (Mw), lower polymerization shrinkage, more rapid hardening and production of stronger and stiffer polymer matrix (Du and Zheng, 2008). However, its desirable properties are partially negated by a relatively high viscosity and low mobility that could affect to the degree of conversion (Du and Zheng, 2008, Filho *et al.*, 2008). Thus, low viscosity diluent monomer, such as TEGDMA, is added to thin down the polymer composite and at the same time increase the degree of conversion and the filler incorporation (Kim and Shim, 2001). Modern composites always comprised with UDMA monomer, which has a molecular weight nearly equal to that of BisGMA, but are less viscous and relatively lower water uptake (Du and Zheng 2008). Furthermore, a greater flexibility of urethane linkage may improve the toughness of composite (Asmussen and Peutzfeldt, 1998). Methacrylate monomers react via an

addition polymerization reaction to form a highly cross-linked structure when light of appropriate wavelength and intensity is applied. Each dimethacrylate demonstrates different properties such as molecular weight, polarity, polymerization shrinkage and viscosity. Although many attempts have been done to replace the commonly used monomers with a new monomer, but the present dental composites continue to be BisGMA, TEGDMA and UDMA based (García *et al.*, 2006, Filho *et al.*, 2008).

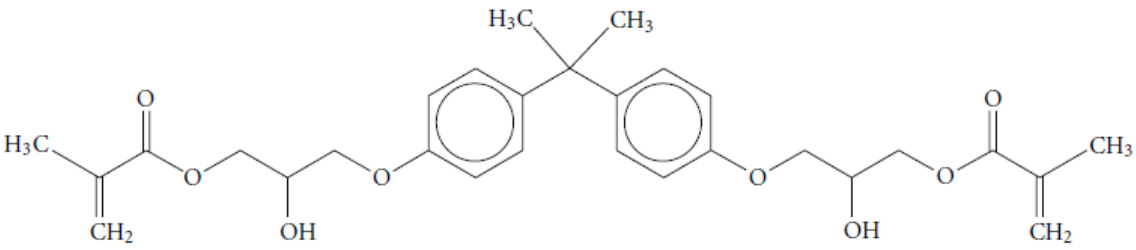


Figure 2.2 a: Chemical structure of BisGMA (Mw=512.6)

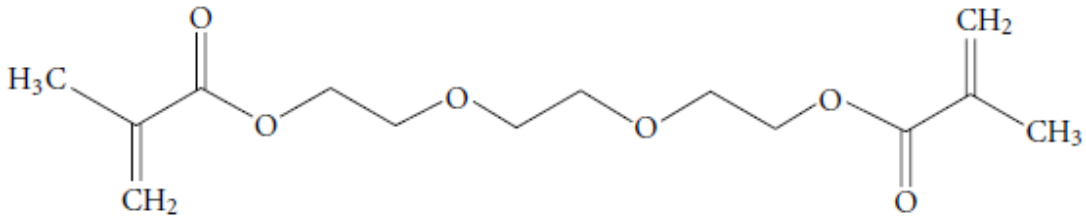


Figure 2.2 b: Chemical structure of TEGDMA (Mw= 286.3)

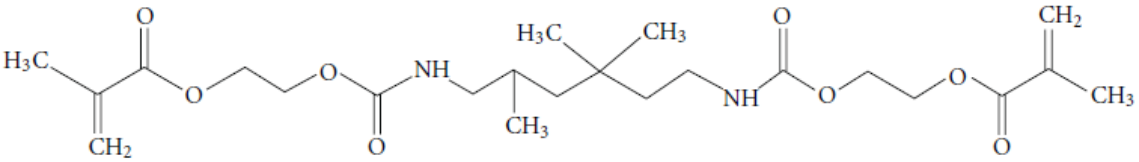


Figure 2.2 c: Chemical structure of UDMA (Mw= 470.6)

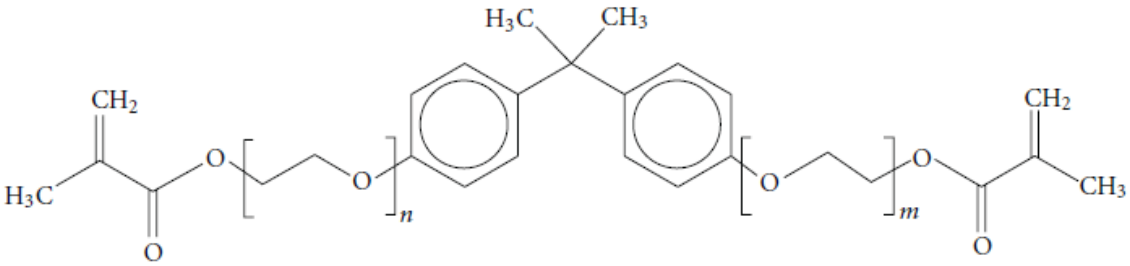


Figure 2.2 d: Chemical structure of BisEMA (Mw= 540)

Figure 2.2 a-d: Dimethacrylates mostly used in restorative dental composites

2.3.2 Filler

Unfilled composite is not suitable to be used in restoration as it demonstrates unsatisfactory properties required. The primary purposes of incorporation of fillers are to provide strengthening a composite and to reduce the amount of matrix material. Several important properties of dental composites are improved by increased filler loading: 1) reinforcement of the polymer matrix, resulting in increased hardness, strength and stiffness, 2) reduction in polymerization shrinkage, 3) reduction in thermal expansion and contraction, 4) improved handling, 5) reduction in water sorption, softening and staining, and 6) increased radiopacity and diagnostic sensitivity (Anusavice, 2003).

In order to ensure the aesthetic of composite restoration, the translucency of the filler must be nearly similar to the tooth structure. Therefore, the refractive index of the filler must be closely matched to the monomers used, which have refractive indices of about 1.5. Most of glasses, quartz and silica that are used for fillers have refractive indices of approximately 1.5, which are adequately achieve sufficient translucency (Anusavice, 2003).

The incorporation of an element of relatively high atomic number or weight into the inorganic filler phase such as barium, strontium and zirconium makes the composite opaque to x-rays (Bowen and Cleek, 1969). The radiopaque restoration material is essential to allow clinicians to diagnose secondary caries and to evaluate the contours, voids and contacts with the adjacent teeth radiographically (Amirouche *et al.,* 2007). Modern composite systems contain fillers such as quartz, silica, silica glass containing barium, strontium and zirconium. The type and size of filler used has been employed as a basic for classification of modern dental composites (Table 2.2).

Table 2.2: Classification of dental composite by filler particle size (modified from Soh *et al.*, 2006)

Type	Filler size (μm)
Macrofill	10-100
Midifill	1-10
Minifill	0.1-1
Microfill	0.01-0.1
Nanofill	0.005-0.01
Hybrid	1-5 and 0.04

The latest classification of composite is nanofilled or nanocomposite which was introduced in 2003. The improvements related to the nanocomposite are discussed in 2.7. By definition, a 'nano-material' possesses components and/or structural features, such as fibres or particles, with at least one dimension in the range of 1-100 nm and subsequently demonstrates novel and distinct properties (Mitra *et al*., 2003, Scientific Committee on Consumer Products, 2007). It is interesting to note that the size of fillers present in microfilled composites do not differ vastly from 'nanofilled' composite. However, these composites lack the high strength needed to emulate amalgam or to be used involving occlusal surfaces, which make them eliminated from the term as nanofilled composites. Another type of composite is called hybrid composites, which having at least two distinct filler size distribution in composite system.

2.3.3 Coupling agent

In dental composite, in which no chemical bond exists between the polymer matrix and the filler particles, coupling agents are used to provide a bond and improve adherence between matrix and filler. Formation of strong covalent bond is very important in obtaining good mechanical properties of restorative dental composites (Soh *et al.*, 2006). The most commonly coupling agent used in silica based

composite is γ-methacryloxypropyltrimethoxysilane (γ-MPS) (Kim and Shim, 2001, Rüttermann *et al.*, 2008, Chung *et al.*, 2009, Kim *et al.*, 2007b, Atai *et al.*, 2004).

In the presence of water, the methoxy groups (-OCH_3) are hydrolyzed to silanol (-Si-OH) groups that can be bond with other silanols on the filler surfaces by formation of a siloxane bond (-Si-O-Si). The organosilane methacrylate groups form covalent bonds with the resin when it is polymerized, thereby completing the coupling process (Figure 2.3) (Anusavice, 2003). Other coupling agents which are often been used in preparing dental composite are 3-aminopropyltriethoxysilane (APTES) (O'Donnell *et al.*, 2009) and γ-glycidoxypropyltrimethoxysilane (GPS) (Chen *et al.*, 2006).

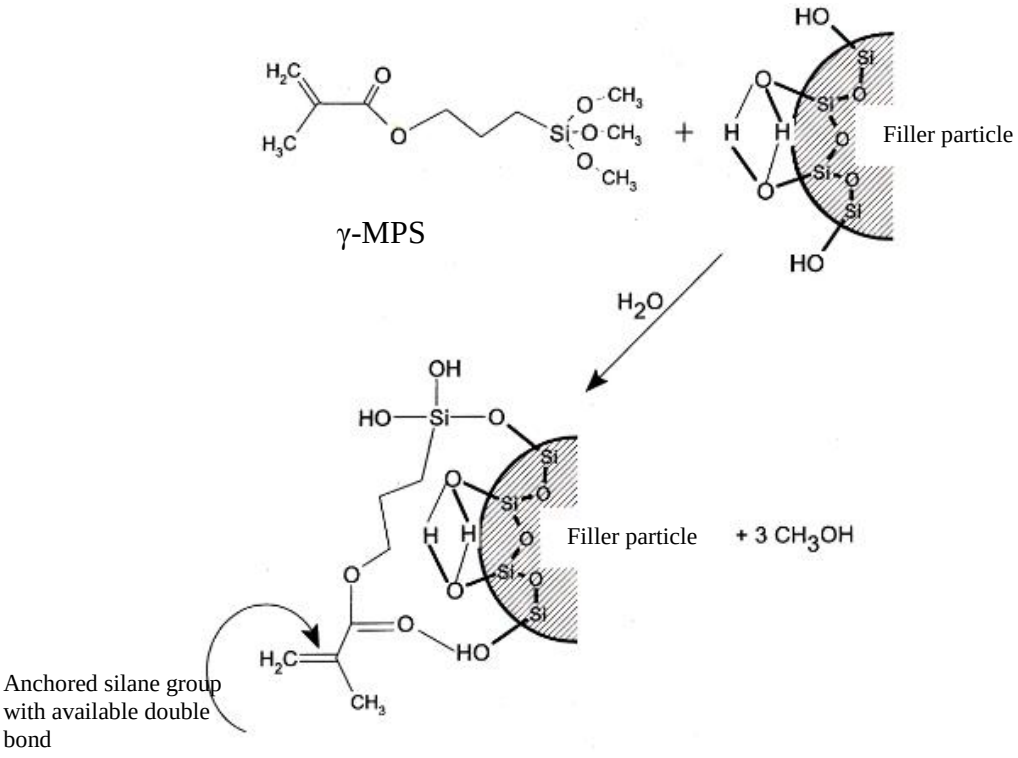
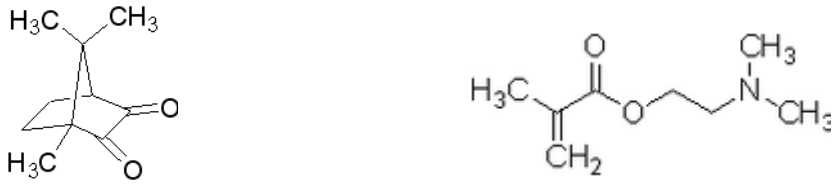


Figure 2.3: Mechanism of surface modification of filler particle by γ-MPS (Anusavice, 2003)

2.3.4 Photoinitiator system

Today, visible light-cured composites are widely used than are chemically activated composite materials. The light-cured composites undergo polymerization by irradiating a blue light curing unit in the wavelength range of 410-500 nm. The

composites contain of photoinitiator system that involves a diketone, such as camphorquinone (CQ), and a reducing agent, such as N,N-dimethylaminoethyl methacrylate (DMAEMA). CQ absorbs the blue light in the wavelength of 450-500 nm range, and creates an excited state that reacts with DMAEMA to produce free radicals that initiate the cross-linking polymerization (Soh *et al.*, 2006).



(a) (b)

Figure 2.4: Chemical structure of photoinitiator system (a) camphorquinone and (b) DMAEMA

2.4 Polymerization process of dental composites

Most of dental composites are polymerized through addition polymerization. Addition polymerization is defined as a reaction between two molecules produce a larger molecule without the elimination of a small molecule, such as water (van Noort, 2002). There are four main stages consisted in addition polymerization, which are activation, initiation, propagation and termination. Ethylene, $H_2C{=}CH_2$ the simplest monomer capable of addition polymerization is used for illustration.

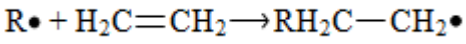
1) Activation

In the visible light-cured dental composites, activation process begin when the free radical-forming chemical, so called photoinitiator generate the free radicals when irradiated to visible light. A free radical is an atom or group of atoms possessing an unpaired electron ($\bullet$). The unpaired electron confers electron-withdrawal ability to the free radical.

$$R{-}R + \text{external energy} \longrightarrow 2R\bullet$$

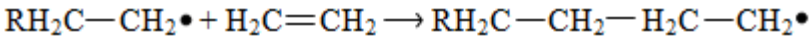
2) Initiation

The initiation process begin when the free radical and its unpaired electron approach to a monomer which containing a high electron density double bond. An electron from that bond is extracted and paired with the R • to form a bond between the radical and the monomer molecule, leaving the other electron of the double bond unpaired.



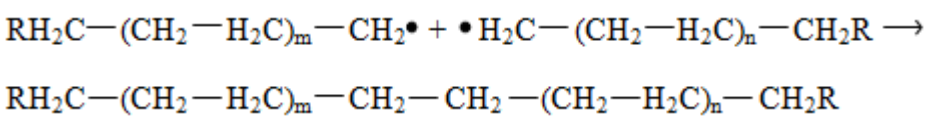
3) Propagation

The resulting free radical-monomer complex then acts as a new free radical center when it approaches another monomer to form a *dimer*, which also becomes a free radical. This reactive species can add to a large number of molecules so that the polymerization process continues through the propagation of the reactive center.



4) Termination

Polymerization reactions are most terminated by direct coupling of two free radical ends or by the exchange of a hydrogen atom from one growing chain to another.



2.5 Photopolymerization of dental composite with visible light curing unit (LCU)

Presently, almost all clinicians use visible light curing unit for restorative dental composite to undergo photopolymerization. There are four main types of light curing units that have been developed including quartz tungsten halogen (QTH) lights, light emitting diodes (LED) units, plasma-arc lights (PAC) and argon laser lights.

Between these types of curing units, QTH lights and LED units are the most frequently used in daily clinical practice.

QTH lights have a quartz bulb with a tungsten filament that irradiates both UV and white light that must be filtered to remove heat and all wavelengths except those in the violet-blue range, between 400-500 nm (Anusavice, 2003). Due to the heat generated, a cooling fan is incorporated together with the slots in the casing for air flow, which causes a noise to the units (Wiggins *et al.*, 2004). In addition, the components of halogen bulbs also tend to degrade over time due to the high operating temperatures and results the reduction of LCU's curing effectiveness. Consequently, dental composites will be less polymerized and result with poorer mechanical properties and increase the risk of premature failure of restorations (Stahl *et al.*, 2000).

A solid-state light emitting diode (LED) technology has been proposed for curing light-activated dental composites. LED units emit radiation only in the blue part of the visible spectrum between 440 and 480 nm and do not require filters. These lights also require low wattage, can be battery-powered, generate no heat, and are quiet because not having a cooling fan (Anusavice, 2003). Although the first generation of LED units provide lower intensity compared with QTH lights, the new technology of high powered LED lights capable of delivering a power density of about 1000 mW/cm^2. Therefore, more efficient curing could be expected and the curing time is also reduced (Stahl *et al.*, 2000). Recently, 3M ESPE has introduced the latest high powered LED units, so called Elipar FreeLight 2 which delivering a light intensity approximately at 1000 mW/cm^2.

2.6 Classification of restorative dental composite

The properties of restorative dental composites are considerably influenced by the inorganic filler particles, therefore the classification of polymer composites always been referred to the fillers that are employed. Although various classifications have been developed, the most commonly used classification method is based on filler particle size. According to filler particle size, four types of polymer composites can be described which are traditional composite, small particle filled composite, microfilled composite and hybrid composite (Anusavice, 2003, Curtis *et al.*, 2008).

Traditional composites [Figure 2.10(a)], which are also referred as conventional or macrofilled composites, are those were developed during the 1970s. Macrofilled composites, filled with 70 to 80 wt% filler content with a mean filler size approximately 8 to 12 μm, and a largest particle size of 50 μm. The macrofillers are mechanically prepared by grinding larger particles of radiopaque glass, quartz, or ceramics into smaller particles. Macrofiller particles are purely inorganic and usually splinter-shaped. These composites exhibit excellent strength and relatively long-term service, but they have a drawback in that the surface smoothness of these restorations is poor, which reduce aesthetic properties and promote plaque adhesion (Anusavice, 2003).

Small particle filled composites [Figure 2.10(b)] were then developed in an attempt to achieve surface smoothness of microfilled composites, and yet retain or improve on the physical and mechanical properties of traditional composites. The inorganic fillers are ground to a size smaller than those used in traditional composites, ranges from 0.5 to 3 μm. Quartz or glasses that contain heavy metals were incorporated with small amount of silica fillers (5 wt%) to adjust paste viscosity. The composites exhibit superior in physical and mechanical properties and indicated for applications

which large stresses and abrasion might be encountered, such as in Class I and II (Figure 2.5 and Figure 2.6). The surface smoothness and wear resistance of composites is improved by the use of small and highly packed fillers, as compared with traditional composites but not as good as microfilled composites. Polymerization shrinkage is comparable to or less than that of traditional composites (Anusavice, 2003).

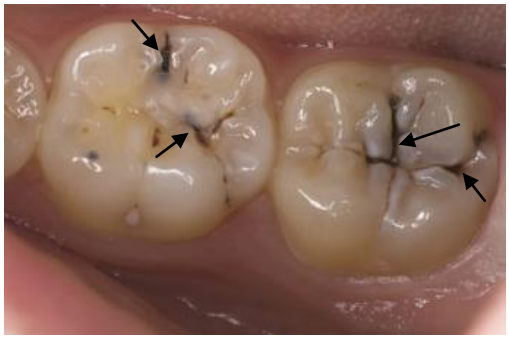


Figure 2.5: Class I caries (Fillings, 2011)

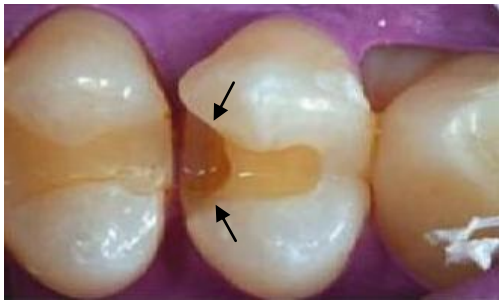


Figure 2.6: Class II caries (Lowe, 2008)

In an effort to overcome the problem of high surface roughness associated with traditional composites, a class of materials that use silica particles as inorganic filler was developed. The first microfilled composites were introduced in the late 1970s contain silica with an average particle size approximately 0.04 μm. Although the composites exhibited very smooth surface finish, the high surface area of silica limit the filler loading up to 20 vol.%. Therefore, a two-stage procedure for the incorporation of filler has been developed to ensure an adequate filler loading. Firstly, a very high filler loaded material so called prepolymerized filler is produced,

then polymerized and ground into particles of 10-40 μm in size. The material is subsequently used as fillers for more resin with incorporation of small percentage of silica [Figure 2.10(c)] (van Noort, 2002). However, the filler loading that can be achieved is still considerably less (~50 vol.%). Due to the lower filler content percentage, microfilled composites have physical and mechanical properties that are inferior to those of traditional composites and not suitable for use as stress-bearing surfaces. Because of their smooth surface, they have become a choice for aesthetic restoration of anterior teeth or restoring smooth surface caries lesions (Classes III and V) (Figure 2.7 and Figure 2.8) (Anusavice, 2003). Example for these composites including Durafill® VS (Heraeus Kulzer), Filtek™ A110 (3M ESPE), Heliomolar® HB (Ivoclar Vivadent), and Renamel® Microfill (Cosmedent).

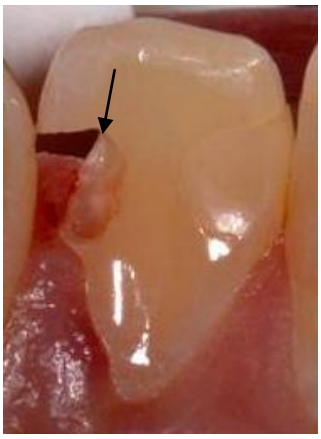


Figure 2.7: Class III caries (Direct Restorations-Class III Composite, 2011)

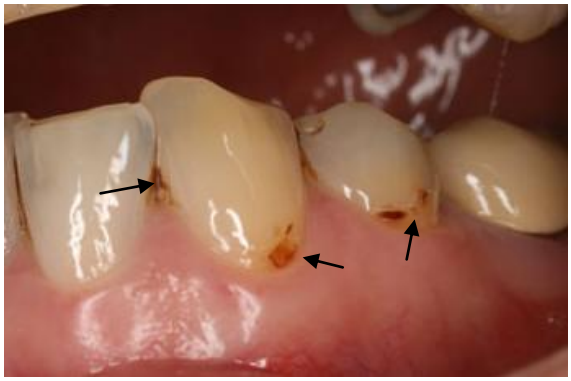


Figure 2.8: Class V caries (Fillings, 2011)

The hybrid composites [Figure 2.10(d)] consist of at least two distinct filler size distribution in the matrix, namely ground particles of glasses containing heavy metals, size ranged from 1 to 5.0 μm and also silica with approximately 0.04 μm of size. The average particle size of hybrid composites is usually > 1 μm (Sensi *et al.*, 2007). The composites usually filled with 70-80 wt% and also incorporated with silica which represents 10 to 20 wt% of the total filler content. The smaller particle size distribution fills in the spaces left between the larger filler particles, which increase the packing density. Physical and mechanical properties for these composites generally range between those of the traditional and small particle-filled composites, and generally superior than microfilled composites. These composites are widely employed for both anterior and posterior restorations, including Class IV sites (Anusavice, 2003). Some examples of hybrid composites include: Z100™ (3M ESPE) and Prisma® APH® (Dentsply).

Figure 2.9: Class IV caries (Direct Restoration-Class IV Composite, 2011)

Modern hybrid composites, so called microhybrid composites, having an average filler particle size of less than 1.0 μm (Sensi *et al.*, 2007). Their working characteristics are about as good as the hybrid composites, and their superior aesthetic and high polishability make them useful for anterior restoration. Fillers in most microhybrid composites are ground glass particles which morphology is irregular (Lu *et al.*, 2006). Some of the available microhybrid composites are:

Charisma® Opal (Heraeus Kulzer), Spectrum® TPH®3 (Dentsply), and Point 4™ (Kerr Corporation).

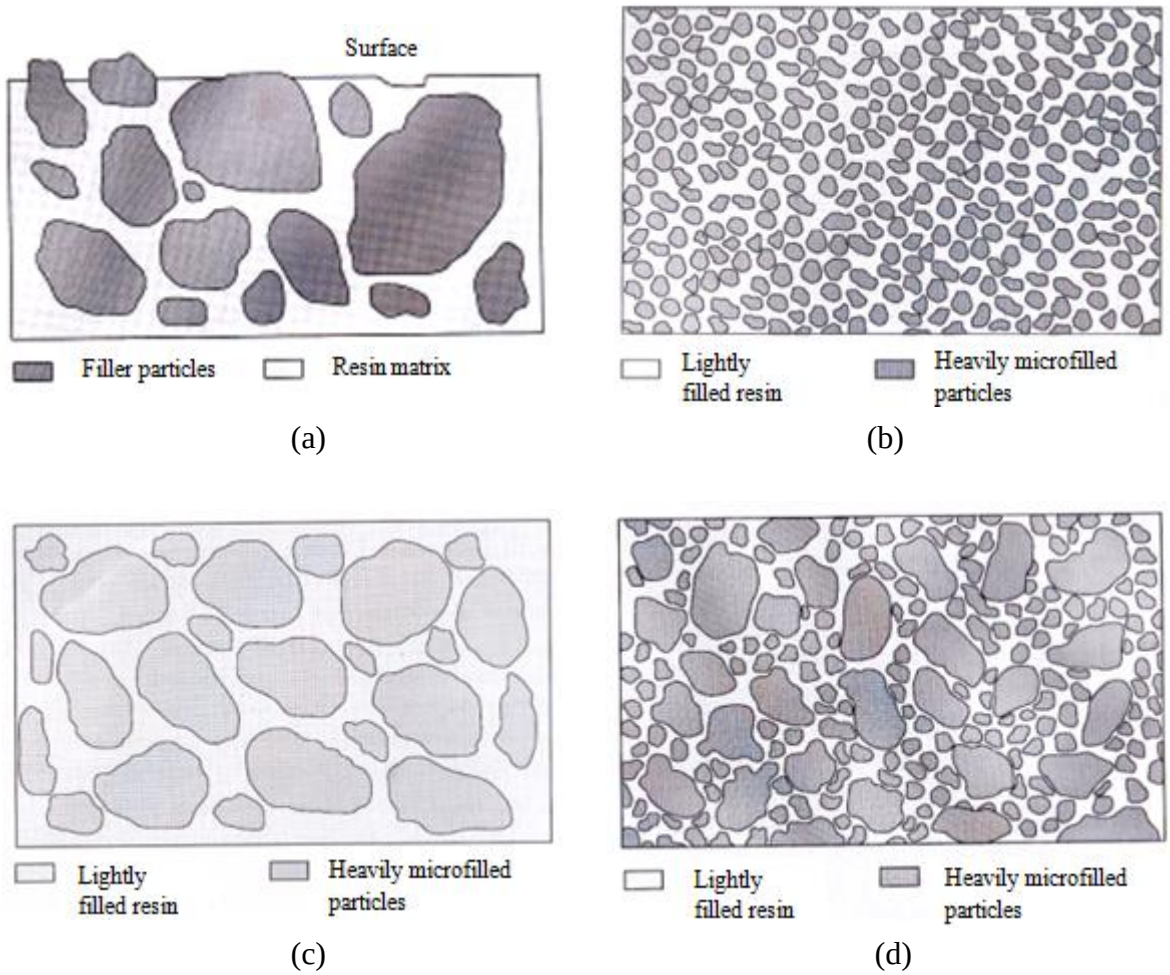


Figure 2.10: Schematic representations highlighting (a) macrofilled composite, (b) small particle composite, (c) microfilled composite and (d) hybrid composite (van Noort, 2002)

2.7 Nanofilled resin composite

The recent introduction of so called nanofilled resin composite or nanocomposite in early 2000 is a new generation of restorative dental composite and becoming more popular in clinical practice. Incorporation of nanofillers with a size in the range of 0.1-100 nanometers in polymer matrix may manipulate the structure of materials, which provide significant improvements in mechanical and optical properties, polishability as well as gloss retention (Mitra *et al.*, 2003).

Nanocomposites differ from the current dental composites, in which they provide enhanced properties at comparatively low filler loading. For comparison purposes, 1 % and 2 wt% of nanosilica filler is assumed to be comparable to 10 % and 20 wt% of microsilica filler (Leng *et al.*, 2007). Nanofillers also capable of increasing the overall filler level by fitting into spaces between other particles in a composite. The increase in filler level will significantly reduce the effect of polymerization shrinkage and dramatically improve the mechanical properties (Soh *et al.*, 2006).

Other advantages of nanocomposites are their superior translucency and deliver optimal aesthetic. The inability of nanofillers to be scattered or absorbed by visible light due to their size below the wavelengths of visible light give benefit to researchers to construct various shades and opacities of dental composites (Kim *et al.*, 2007a).

In addition, incorporation of nanofillers provides the high polishability, just like typical microfilled composites. Although it is said that microhybrid composites already provide sufficient surface polish, but the issue still arise relating their high surface roughness after period of times when these materials are applied in clinical application (Mitra, 2005).

There are two approaches in order to produce inorganic nanofillers, which are top-down approach and bottom-up approach. The top-down approach is when macroscopic fillers are downsized by physical means, such as mechanical grinding or high energy milling. However, there are limiting factors to this approach, as fillers become irregularly-shaped and sizes below 500 nm are hardly generated. On the other hand, the bottom-up approach starts at the other end: materials and phases are generated by the physical or chemical means from precursor compounds forming

nanoscale fillers, allowing the production of round-shaped fillers less than 100 nm in diameter, such as those observed on nanocomposites (Moraes *et al.*, 2009).

Filtek™ Supreme and Filtek™ Z350 are such examples of nanocomposites developed by 3M ESPE using unique nanofillller technology, formulated with nanoparticles and nanocluster filler particles. Nanoparticles or also known as nanomers are monodisperse nonagglomerated and nonaggregated silica particles of 20-75 nm in dimension. Nanocluster fillers are defined as loosely bound agglomerates of nano-sized particles with average size particle of 1 μm which were prepared by lightly sintering nanomers to form clusters. Unlike dense hybrid filler particles, these agglomerated clusters are porous structured which allow the resin matrix to fill the spaces within and between the clusters (Mitra, 2005).

2.8 Preparation of dental composite

In preparation of dental composites, the selection of monomers ratio is very important as they may affect the performances of composites. Usually, manufacturers would combine at least two types of monomers, which are base monomer e.g. BisGMA, UDMA, BisEMA and also diluent monomer e.g. TEGDMA (Anusavice, 2003). Asmussen and Peutzfeldt (1998) claimed the selection of monomers ratio is depending on the intended uses of dental composite. In many cases, high stiffness and strength are the most desirable for preparing dental composite, but in certain circumstances flexibility may be the property of interest. From their study, thirty types of composites containing different ratio of TEGDMA, BisGMA and UDMA monomer mixtures were prepared and their diametral tensile strength, flexural strength and modulus were evaluated. They reported the substitution of BisGMA or TEGDMA by UDMA resulted an increase in tensile and

flexural strength, whereas the substitution of BisGMA by TEGDMA increased tensile, but reduced flexural strength.

Another study by Emami and Soderholm (2009), claimed the high concentration of BisGMA provides a strength for composite, however higher viscosity from BisGMA will slow down filler sedimentation and make the filler incorporation more cumbersome. Therefore, TEGDMA is incorporated to facilitate filler addition and improve conversion level. However, the high concentration of TEGDMA will lead to the greater polymerization shrinkage and reduce the stiffness of composite. It shows that both base and diluent monomers give an opposite effect on properties of composite. Therefore, many studies (Urabe *et al.*, 1999, Xu, 1999, Atai *et al.*, 2004, Veranes *et al.*, 2006, Samuel *et al.*, 2009) suggested the proportion between base and diluent monomer should be relatively the same (50:50 or 60:40). Throughout this study, the proportion of monomers (BisGMA:UDMA:TEGDMA) used was 30:20:50 based on Asmussen and Peutzfeld (1998), which gave the most appropriate mechanical properties to the composites.

Previously, 3M ESPE has introduced a new type of monomer resin called as silorane resin, which is derived from the combination of the two chemical building blocks of siloxanes and oxiranes. The silorane ring-opening monomers provide for low polymerization shrinkage without compromising physical and handling properties. The company claimed the volumetric shrinkage of Filtek™ Silorane Low Shrink Posterior Restorative resin is less than 1 %, lower than the 2 to 5 % exhibited by dimethacrylates composites (Filtek^{TM} Silorane, 2007).

Major developments of restorative dental composites come from the improvement in filler systems. Material's strength, elastic modulus, hardness, shrinkage and wear resistance are greatly influenced by the filler loading of composites. In determining